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Atmospheric Chemistry and Physics Discussions

Interactive comment on "First remote sensing measurements of ClOOCl along with ClO and $ClONO_2$ in activated and deactivated Arctic vortex conditions using new ClOOCl IR absorption cross sections" *by* G. Wetzel et al.

Anonymous Referee #1

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The authors use Arctic stratospheric limb emission measurements from two flights of the balloon-borne MIPAS-B to determine mixing ratios of ClONO2, ClO, and ClOOCl. New lab measurements of IR cross sections of ClOOCl are presented and used to retrieve the ClOOCl mixing ratios. The results are compared with simulations from the chemistry climate model EMAC. The ClOOCl equilibrium constant is also calculated and reported. The manuscript content is certainly within the scope of the journal, and the material is presented in a clear, concise, and well-structured way. However, there are significant issues, detailed below, which need to be addressed.

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1) Measuring ClOOCl with this technique is clearly a challenge, and I would like to see some clarifications in this paper that there is actually the capability here to make this measurement in a statistically significant way. The authors initially present radiance simulations to demonstrate the capability of MIPAS-B to detect ClOOCl. But the spectral window tested (721-788 cm-1) is significantly larger than the spectral region used in the retrieval calculations (755-788 cm-1). The use of a number of grid points in the wide spectral window tested allows for higher signal to noise. The simulation results presented in Table 1 seem irrelevant to the capability of MIPAS-B to detect ClOOCl using the narrower, experimental spectral window for the flight presented here. The simulation should be shown with the spectral region actually used in flight.

Reinforcing the concern about the ClOOCl measurements are the results in Figure 9. The authors acknowledge that there are significant interferences in the residual spectra but state that it is the gradually changing shape along the frequency scale that provides evidence of ClOOCl. This difference is only evident when comparing two calculated spectra (one with and one without ClOOCl) and is not apparent when using the measurements. The difference between the calculated spectrum and the measured spectrum ($\sim$5-20 shown in Figure 9b) is significantly greater than the difference in the two calculated spectra used to show the trend (<1 shown in Figure 9d). The authors state in line 24 of p. 20115 that the introduction of ClOOCl emission into the retrieval "slightly improves the root of mean squares of the residual", but more quantitative detail is necessary: Is the 0.27% difference in the root of mean squares between Figures 9b and 9c actually significant? More convincing evidence needs to be presented here that the extremely small ClOOCl signal being identified from a relatively huge background (Figure 9a), is actually significant given the uncertainties of the instrument and the fit.

2) ClOOCl IR cross sections. The number density determination here is critical in ensuring that the new cross sections are correct. The authors state that a check on their FIR results was done by calculating the titrated amount of Cl2O (lines 17-19, p. 20111), and they use this as the basis for essentially saying that it is "impossible" for the

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previous work of Brust et al. to be correct (lines 15-18, p. 20112). The authors need to include more detail about how the Cl2O titration measurement was made and what the uncertainties are. A small error in the Cl2O measurement can translate into a big error in ClOOCl number density, e.g., a difference of 20% vs 30% in Cl2O represents a 50% change in ClOOCl.

Since the Cl and Cl2O were mixed prior to being cooled (line 6, p. 20110), there is reason to believe that the ClO bimolecular reactions produced Cl2 and OClO. Once cooled, Cl2O3 would also be present from ClO + OClO. Moreover, given the somewhat lengthy 50-second residence time, some ClOOCl certainly would have been lost on the walls to form Cl2 and perhaps other products. I would like to see more discussion on the potential impact of chemical impurities on the FIR number density determination.

3) Figure 11. Because ClOOCl is below the instrument detection limit, it is shown to be 0 below 19 km and above 22 km, and then this 0 value is used to calculate ClOx and Cly*res. This seems inappropriate. If ClOOCl is 0.3 or 0.4 ppb, that's a 0.6 or 0.8 ppb impact on ClOx and Cly*res. At a minimum, error bars should be included on ClOOCl at 0 and propagated to the values calculated from it. Alternatively, because the detection limit is so high, just don't show any ClOOCl data points or calculate ClOx and Cly*res when the ClOOCl measurements are below the detection limit.

Figures 12 - 14. Same general issue as raised for Fig 11 above. Just because a measurement is below the instrument detection limit doesn't mean it can be set to 0 with no error bar.

*Additional suggestion/corrections:

Page 20107, Lines 17-22: This sentence needs to be re-written for clarity.

Page 20109, Line 24 – Page 20111, Line 7: This paragraph should be split into 2 or 3 smaller paragraphs.

Page 20110, Line 12-15: What is the source of these high resolution mid infrared

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spectra? The previous sentence only mentions acquiring two low resolution MIR measurements and a FIR measurement in the experimental procedure.

Page 20111, Line 25: change was to were

Page 20114, Line 3: centered is misspelled

Page 20116, Lines 16-18: Please make a more specific statement about the ClOOCl detection limit than "several tenths of ppbv". The lowest reported value shown in Figure 11 is around 0.6 ppb.

Page 20118, Line 27: Either the word dimer should be removed, or it should be changed to ClO dimer

Page 20119, Line 13: there is a missing "l" in Cly* res

Page 20121, Line 2: "established chlorine chemistry" should have a reference or further explanation of what is meant. This paper is initially motivated by discussing the Pope result – a reference back to that here would be appropriate.

Figure 3 caption, Line 4: What does "technical chlorine" mean?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20103, 2009.